MORPHOLOGY AND CHEMISTRY OF TWO ANCIENT WOODS[1]

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ABSTRACT

Wood specimens obtained from rubble ore in iron mines in northern Quebec were shown to be white pine of about 10 million years and probably redwood of about 100 million years. The ancient pine, 0.80 specific gravity, largely retained its structure, but had lost most of its carbohydrate material. Its residual cellulose was amorphous. The lignin was extensively demethylated, and there was evidence of condensed ring structures. In contrast, the older redwood, 1.24 specific gravity, was highly compressed and contained numerous resin beads in the strand and ray parenchyma cells. It consisted almost entirely of lignin, with about two-thirds of the methoxyl content retained, and there was no evidence of coalification.

INTRODUCTION

Two specimens of ancient wood were obtained from depths of about 150 ft embedded in rubble ore in iron mines near Schefferville in northern Quebec. Specimen No. 1, from Ruth Lake mine, was a 10-million-year-old white pine, while Specimen No. 2, from Redmond mine, was a 100-million-year-old conifer, most likely redwood. These specimens were neither petrified nor coal-like. Specimen No. 1 was brown and woodlike in appearance, whereas Specimen No. 2 was harder and darker. Their specific gravities were 0.80 and 1.24, compared with 0.41 and 0.42 for the same species in the green state.

Geological notes provided by W. D. Bullock, engineering superintendent of Iron Ore Company of Canada, Schefferville, Quebec, describe rubble ores at four neighboring mines, in all of which ancient wood has been found. At the Ruth Lake mine, which may be typical, the rubble ores form a large tongue extending from the surface to a depth of 500 ft, within a narrow highly compressed syncline. The breccia is a highly heterogeneous mixture of angular to subangular fragments ranging in diameter from less than an inch to more than 30 ft. The breccia is also remarkable for zones containing large wood fragments at depths ranging from 100 to 400 ft. Some tree stumps were more than 3 ft in diameter. In late Cretaceous times, the stresses of a period of deformation affected particularly the areas of strike fault overlap. Recurrent movements occurred along the original zones of weakness and shearing couples developed, producing cross-folding and fragmentation. It has been suggested that the Ruth Lake Mine ore breccias probably resulted from the rotation and overturning of a plunging dragfold located between two major strike faults. Under these conditions, a small structural basin would be developed, and trees and other material on the surface would fall in, in a manner somewhat analogous to avalanches. The area must have had at least moderate relief; giant earthquakes probably occurred when the pressure was relieved. In post-Cretaceous times, the bedded leached ores with their capping of gravelly rubble ores were again down-

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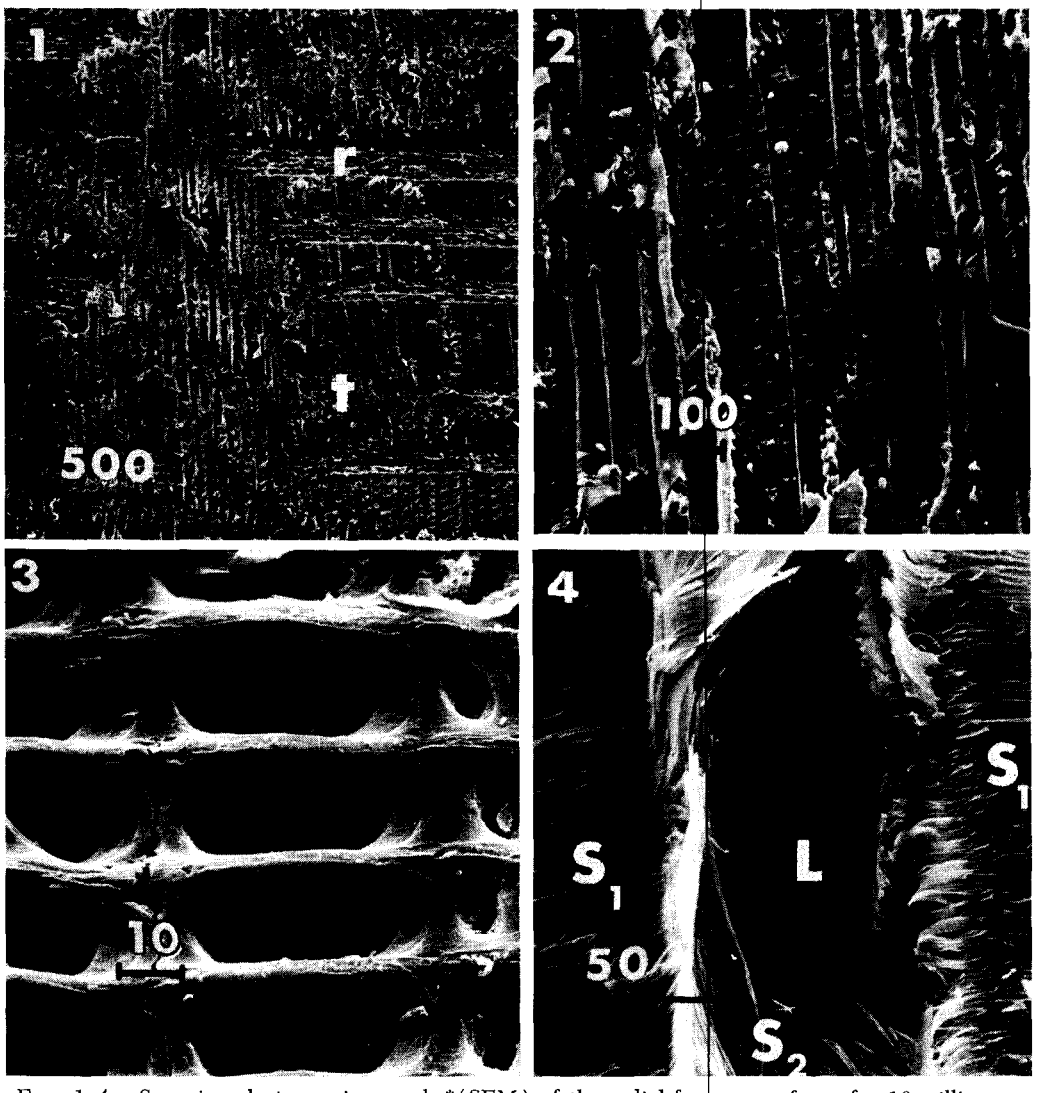


FIGS. 1–4. Scanning electron micrographs*(SEM) of the radial fracture surface of a 10-million-year-old white pine showing: 1. Tubular tracheids (t) and the horizontal rays (r). 2. Longitudinal tracheids displaying intertracheid pitting. 3. Fenestriform ray-tracheid pitting. 4. A tubular tracheid exposing the S_1 and S_2 layers and the inner lumen lining (L) without microfibrillar structure.

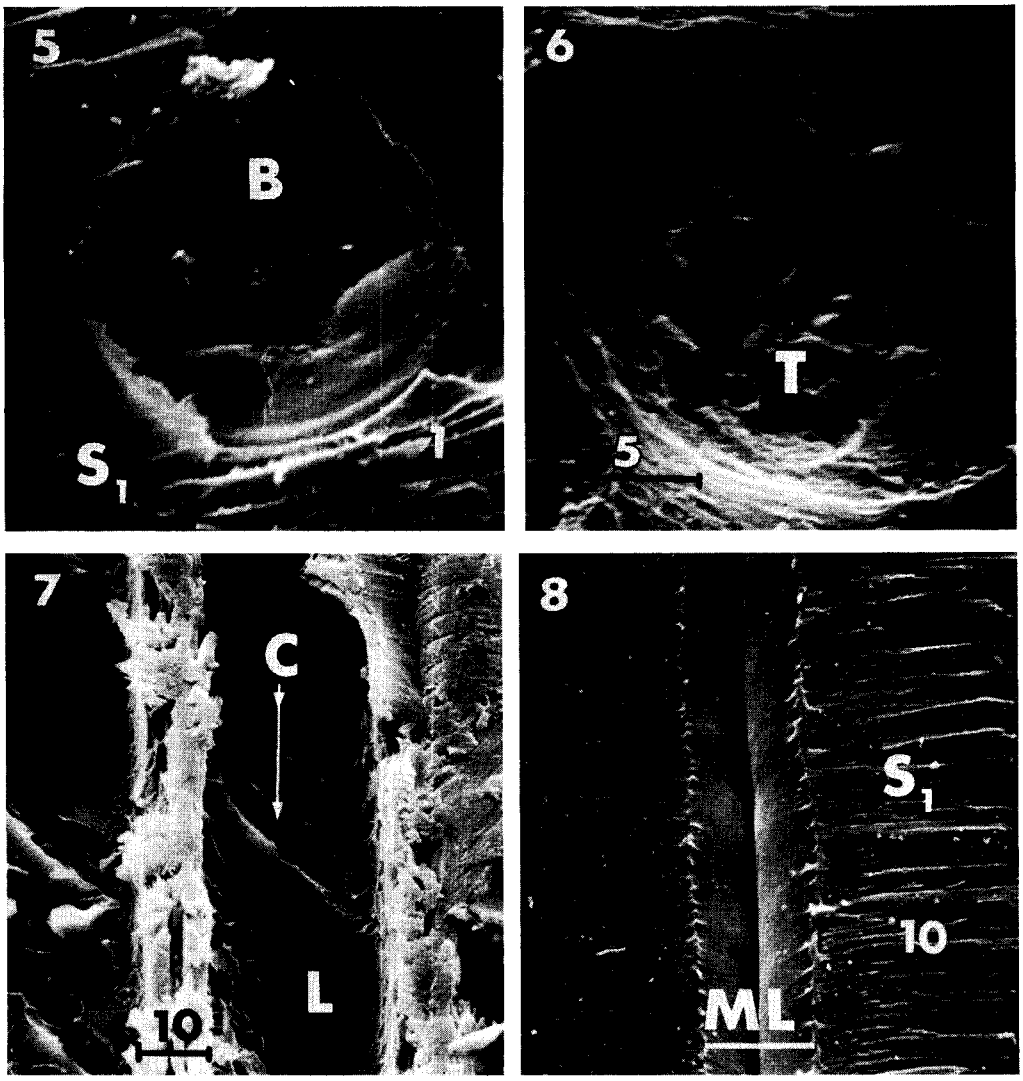
* Scales are in microns in all micrographs.

faulted and then preserved in part from regional peneplanation. The post-Cretaceous peneplanation was very gradual, with no preferential development of valleys. During Pleistocene, the whole area became permanently frozen and the rubbles became very hard—their resistance to erosion was as great as the adjoining rock, and they suffered no appreciable glacial gouge (Usher 1954; Stubbins, et al. 1961).

The age of these specimens made it desirable to determine the physical and chemical properties as well as residual wood and fiber structure.

MATERIALS AND METHODS

Age determinations were made by identification of spores and pollen by Professor Glenn E. Rouse of the University of British Columbia, who reports: "The Ruth Lake



FIGS. 5–8. SEM of a 10-million-year-old white pine showing: 5. S_1 microfibrillar structure and the inner pit border (*B*) of an intertracheid pit-pair. Note the lack of circular microfibrillar structure and the presence of a radial split across the pit aperture and pit border. 6. An intertracheid bordered pit showing torus (*T*) residues of a disintegrated pit membrane. 7. Two longitudinal tracheids split parallel to their long axes, thus exposing their inner lumen lining (*L*) that contains several spiral checks (*C*). 8. Two adjacent longitudinal tracheids exposing S_1 microfibrillar structure and the middle lamella region (*ML*), from which much of the middle lamella substance has disappeared.

sample" (Specimen No. 1) "appears to be Tertiary; I would venture a likely age of Miocene or early Pliocene, but cannot be more precise without better material; it could even be Pleistocene. The Redmond sample," (Specimen No. 2) "on the other hand, is either late Albian or Cenomanian; this is a confident determination (See also Dorf, 1967). However, in an abstract of a paper presented to the Geological Association of Canada in March 1958, Blais and McMahon accepted that both the Ruth Lake and Redmond plant-bearing rubbles were upper Cretaceous in age. There is

little disagreement on the relative age of the Redmond deposits; the main discrepancy is in the age of the Ruth Lake wood. Although these deposits appear to be in relatively similar stratigraphic positions, they clearly represent materials of two distinctly different ages; they were either deposited at different times, or represent material of two different ages laid down at the same time." Our interpretation of this report in terms of millions of years is based on commonly accepted paleobotanical time scales.

Chemical analysis included elementary analysis, methoxyl, holocellulose, α-cellulose, lignin, moisture, and ash. Holocellulose was prepared by the Institute of Paper Chemistry chlorite-acetic acid method, on Specimen No. 1 only. From the holocellulose so prepared, α-cellulose was isolated using TAPPI method T203 05-61. Klason lignin was determined by TAPPI method T13 m-54. Infrared spectra were determined on the two specimens and on the α-cellulose isolated from Specimen No. 1 using the KBr pellet technique and a Beckman IR-9 instrument. Specific gravity was determined by TAPPI method T18 m-53. Resin determination was by TAPPI method T204 05-69.

In addition to the above determinations, the morphology of the two specimens was studied by scanning electron microscopy. For this the specimens were first fractured in the radial, tangential, and transverse planes, and were subsequently mounted onto standard aluminum stubs. These were then coated with a layer of gold-palladium alloy in a high vacuum evaporator and were subsequently studied in a Cambridge Stereoscan operated at 24 kv.

RESULTS AND DISCUSSION

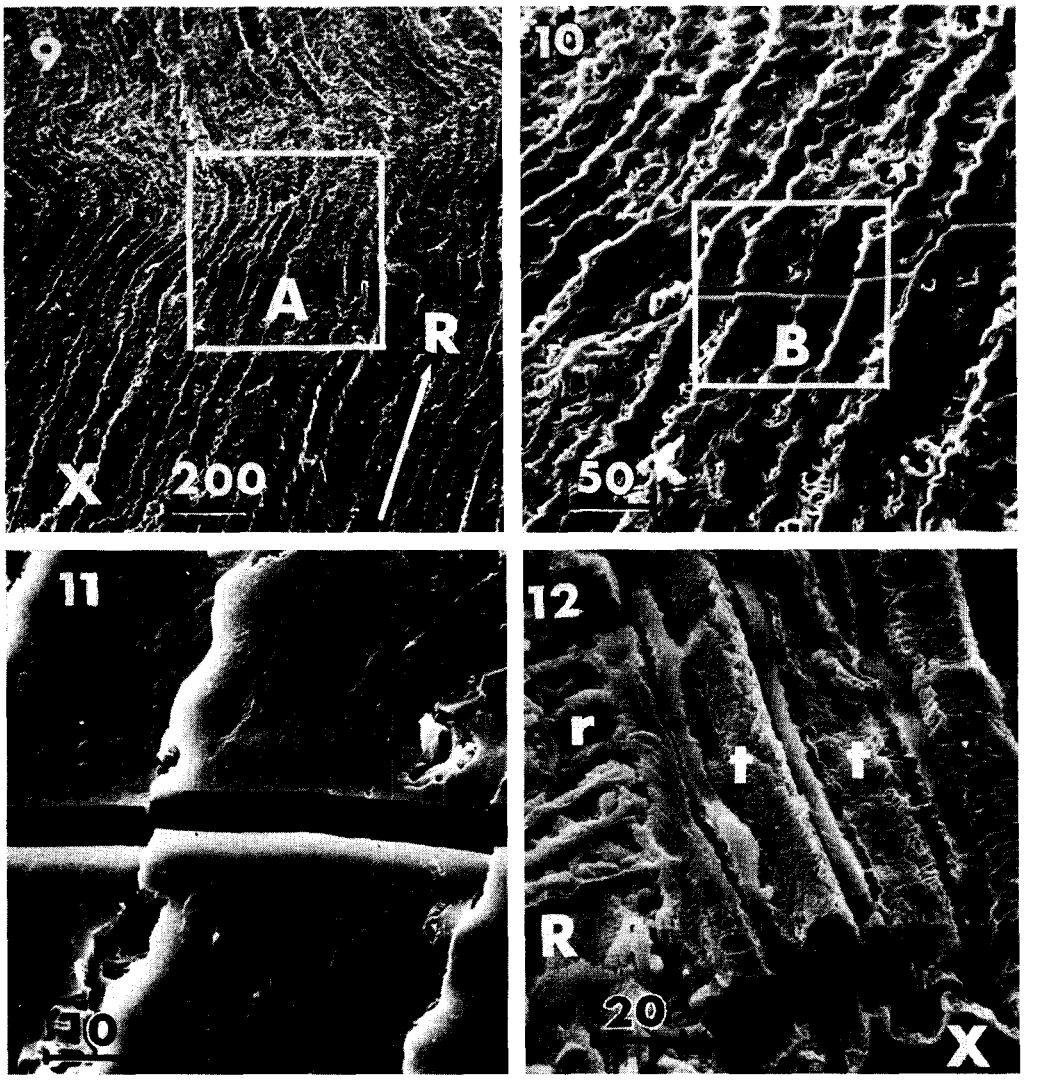
Morphology of ancient white pine

This 10-million-year-old coniferous sample contains resin canals (108 μm in diameter) and possesses fenestriform pitting, but lacks dentations in the ray tracheids. On the basis of these features, this species can definitely be identified as a white pine.

Although the sample has the appearance of charcoal, albeit somewhat browner in color, its overall wood structure is preserved to a relatively high degree. Figure 1, for example, shows a radial view of this specimen exposing the longitudinal tracheids (t) and the horizontal rays (r). These cells maintained their tubular structure, which indicates the absence of an excessive amount of pressure on the specimen over the 10-million-year period.

Both the intertracheid pitting (Figs. 2, 5, and 6) and the fenestriform pitting (Fig. 3) are fairly well preserved, although some degradation is obvious at high magnifications (Figs. 5 and 6). Note particularly the disappearance of the circularly oriented microfibrils from the inner surface of the pit border (Fig. 5) and the development of a split across the same pit border (Fig. 5). Furthermore, intact pit membranes could not be found in any of the pits examined, which means that these have degraded almost completely, leaving behind some torus (T) residues (Fig. 6).

The various layers of the tracheid wall are preserved to varying degrees. The microfibrillar structure of the S_1 layer, evident on the greatest part of the fracture surface (Figs. 4, 5, and 8), and the S_2 layer (Fig. 4) appear quite intact. However, the microfibrillar structure of the S_3 layer could not be identified in any of the areas examined (Figs. 4 and 7). This suggests that while the S_1 and S_2 layers are fairly well preserved, the S_3 layer seems to be at least partially degraded. This seems logical since S_3 is the layer that lines the lumina of the tracheids. Therefore, this is the layer to be attacked first, or oxidized by the oxygen contained in the lumina of tracheids. Briefly, the partial degradation of the tracheid wall is confirmed by (1) the presence of numerous spiral checks in the tracheid wall, such as the ones seen in Figs. 5 and 7, (2) the breakdown of the pit membrane (Fig. 6), (3) the absence of any microfibrillar structure in the lumen lining (Figs. 4 and 7) and on the inner pit border (Fig. 5), and (4) by a significant decrease in cellulose content (Table 1).



FIGS. 9–12. SEM of a 100-million-year-old conifer sample exposing: 9. Radial rows of what were originally tracheids in the transverse plane (*X*). *R* indicates the radial direction. 10. Enlarged view of area *A* in Fig. 9 showing the lack of tracheid luminae or any tracheid structure. 11. Enlarged view of area *B* in Fig. 10 showing a straight and brittle fracture across the radial rows of tracheids without following the tracheid contours. 12. Individual tracheids (*t*) and rays (*r*) exposed in the radial plane (*R*).

Table 1 reveals 22.3% cellulose in this specimen. This value is about one-half the accepted value for cellulose content of this species. This decrease accounts for the partial degradation of cellulose in the secondary wall and possibly in the primary wall. The lignin content of this sample was found to be much higher than that of normal wood, although part of the lignin from the middle lamella region seems to have been removed (Fig. 8).

The types of degradation could include oxidation, thermal degradation, and possibly bacterial attack. The spotlike areas seen on the inner pit border of Fig. 6 could possibly be the result of bacterial attack.

The possibility of this specimen being

compression wood was considered and eliminated on the basis of light microscopic observations. The tracheids in cross-sectional view appear angular in outline, rather than round as in compression wood, and intercellular space is less common than that in compression wood. Although spiral checks are present in the tracheid walls, the microfibrillar orientation in the S_2 layer is similar to that in normal tracheids.

Morphology of the 100-million-year-old conifer

This specimen possesses the color of black charcoal, but displays a very high degree of sheen on a freshly fractured surface. It is very brittle in nature and possesses a high specific gravity, 1.24, as compared to that of an average coniferous wood (0.45).

The specimen reveals radial alignment on the transverse surface (Figs. 9 and 10), which suggests that it is a coniferous species. It possesses high rays (maximum counted 19 cells), lacks vertical and horizontal resin canals, and both the rays and the longitudinal parenchyma cells contain numerous spheres of resin beads (Figs. 14 and 16: B). All of these are characteristic features of the species in the Cupressaceae-Taxodiaceae families. However, since more definite identification features such as color, pitting in the ray contact area, intertracheid pitting, texture, and the nature of transition from earlywood to latewood have not been preserved, the definite identification of the species within these families is not possible. The presence of characteristic resin beads in the longitudinal parenchyma cells suggests that this is most likely redwood.

Although the radial alignment of the wood can still be readily identified (Figs. 9, 10, 15, and 16), the cellular structure of the sample has almost completely disappeared. Only the rays are preserved to some extent, but even in these cells ray pitting can not be recognized (Figs. 15 and 16). The rays appear as parallel wavy lines on the radial surface (Figs. 15 and 16) in between the radial rows of tracheids.

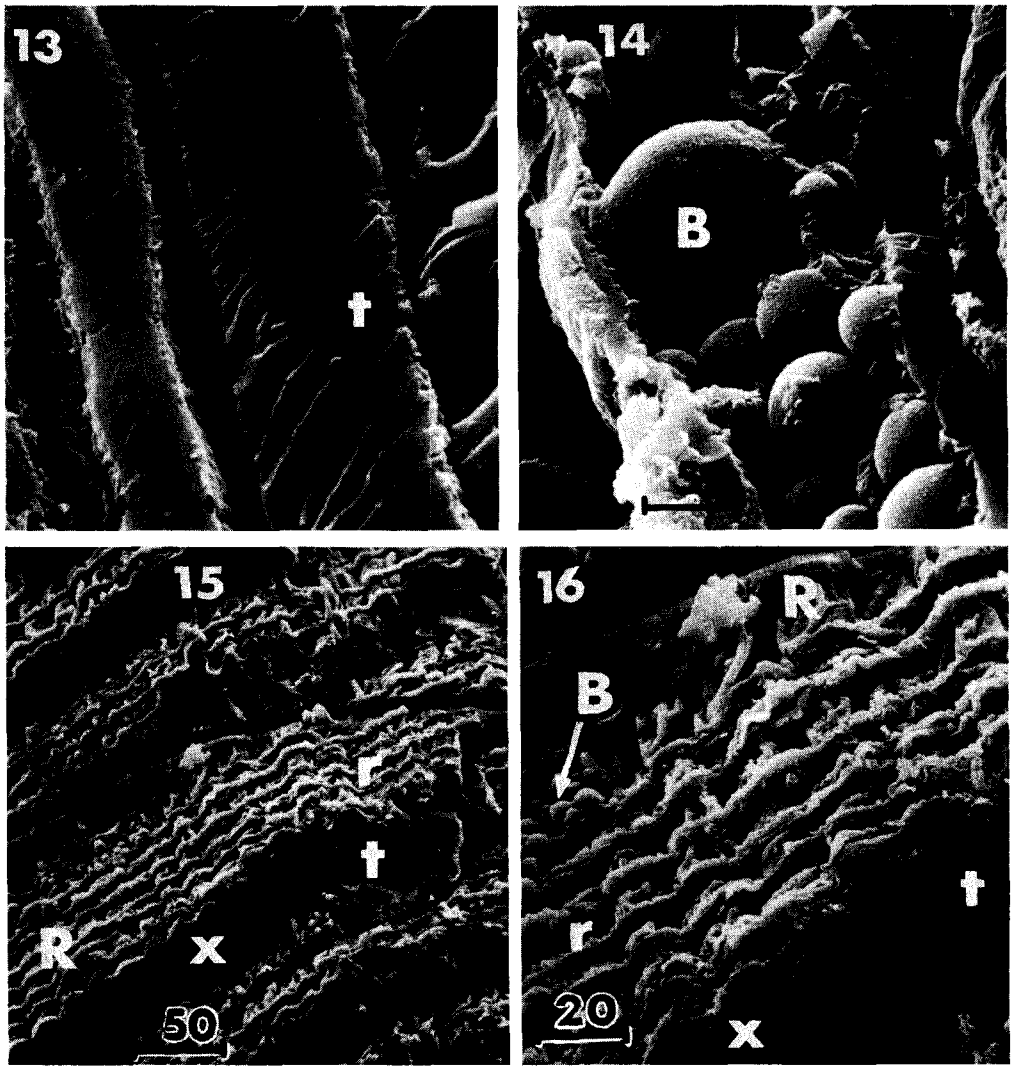
In radial fracture, the plane of fracture closely follows the rays. In fact, fracture seems to occur almost exclusively within the planes of rays (Fig. 15) and avoids the path along the radial rows of tracheids. This also proves that the rays are preserved to a greater extent than the tracheids.

It is clearly seen that some of the ray cells and many of the longitudinal strand parenchyma cells are filled with spheres of resin (Figs. 14 and 16), such as the type normally observed in the species of Cupressaceae-Taxodiaceae families. Their presence is confirmed by the chemical analysis, which showed 4.2% resin in the specimen. These seem to be preserved almost completely. It seems likely that the partial preservation of rays, in contrast to the disappearance of tracheids, is also due to their impregnation with such resinous substance.

Figures 9 and 10 show that the only structures that can be identified on the transverse plane are residues of what were originally the radial rows of tracheids. However, the individual tracheids can not be readily identified, nor can their wall structures be seen and even the lumina of the tracheids have completely disappeared as seen in cross-sectional views (X) in Figs. 9 and 10. This is further seen in Figs. 15 and 16 where the radial rows of tracheids (t) appear as solid dark bands between the rays.

The question yet to be clarified is whether the lumina of the tracheids disappeared through the collapse of all cells, or through the deposition of foreign substances. One of these processes must have occurred to account for the high specific gravity increase and for the disappearance of all lumina. The low ash content (2.8%; Table 1) tends to confirm the former possibility.

The fact that the rays appear as wavy lines rather than straight parallel lines (Figs. 15 and 16) strongly suggests that the tree trunk buried deep in the ground was under high pressure over the 100-million-year period. Such pressure could cause the wood cells to collapse, thus eliminating



FIGS. 13–16. SEM of a 100-million-year-old conifer specimen showing the radial fracture surface. 13. Individual tracheid surface (*t*) revealing the lack of any microfibrillar structure. 14. A strand parenchyma cell containing numerous spherical resin beads (*B*) of varying sizes. 15. Fracture surface showing several wavy rays (*r*) in the radial plane (*R*) and cross-sectional views of radial rows of tracheids (*t*) in between without lumina. 16. Enlarged view of Fig. 15 showing spheres of resin beads (*B*) in some ray cells (*r*).

their lumina and increasing the specific gravity of the sample.

The surfaces of this specimen produced in fracture fail to reveal any microfibrillar structure in any of the three planes. This is particularly apparent in Figs. 9 and 10 where a straight break occurred across the radial rows of what were originally tracheids, without following any tracheid contours such as the type found in the fracture of normal wood. In a few cases, however, individual tracheids could be identified in longitudinal fracture. Examples of these are seen in Figs. 12 and 13. Closer examination of these surfaces reveals no microfibrillar structure. This is expected, especially since the chemical analysis revealed no cellulose in the sample.

TABLE 1. *Analyses of ancient wood specimens (ash-and moisture-free basis)*

	Specimen No. 1 white pine 10^7 years old	Specimen No. 2 conifer 10^8 years old	Modern conifer
Specific gravity	0.80	1.24	0.41, 0.42
C	62.7	64.2	50
H	5.8	5.6	6
O (by difference)	28.4	27.4	44
Methoxyl	4.3	10.3	5.2
Methoxyl in lignin	—	—	15.3
"Holocellulose"	38.5	0*	71
"α-cellulose"	22.3	0	43
"Lignin"	80.6	100	29
Resin	—	4.2	—
Ash	3.1	2.8	0.2–0.4
Moisture	4.9	4.5	6.3

* About 2% total sugars indicated by Somogyi test (1952) on filtrate of lignin determination.

Chemical analyses

The results of chemical analyses, compared with accepted values for conifers, are shown in Table 1.

It is evident that these specimens have increased in carbon content and have lost oxygen-containing material. They have also lost methoxyl. The total carbohydrate material has decreased considerably. Specimen No. 1 has a substantial amount of material that behaves as though it were holocellulose in the chlorite method. After six chlorite treatments—three are normally sufficient—38.5% of the specimen was undissolved—"holocellulose"—and after alkaline extraction 22.3% remained as "α-cellulose." The Klason lignin determination gave a value of 80.6%. There is thus considerable overlap between holocellulose and lignin—that is, residual material not attacked by chlorite and insoluble in 72% H_2SO_4. The infrared spectra suggest that there is a small amount of lignin in the α-cellulose. The lignin in Specimen No. 1 is extensively demethylated (about 5% methoxyl compared with a normal value of 15.3% for coniferous lignin) and has apparently undergone other changes that make it less susceptible to attack by chlorite. The data suggest that about 80% of the α-cellulose of the young pine has been lost as well as most, perhaps nearly all, of the hemicellulose. Specimen No. 1 may be regarded as being composed of approximately 20% cellulose and 80% of a lignin that has lost about two-thirds of its methoxyl content. Corrected for moisture and ash, Specimen No. 2 behaves as though it is all, or nearly all, Klason lignin. Specimen No. 2 may be regarded as being composed of a lignin that has lost about one-third of its methoxyl content. Both specimens appear to be a little low in oxygen and a little high in hydrogen compared with normal wood. Ash also is higher than normal, but these woods cannot be considered petrified. Moisture is lower than in normal, air-dried wood.

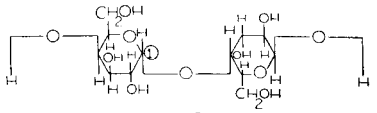
Infrared spectra

The infrared spectra of Specimens 1 and 2 are compared to that of modern spruce wood in Fig. 17. The most noteworthy differences in the spectra are in the region 1000–1200 cm^{-1}. The ancient wood specimens absorb less in this region than does the modern conifer. The absorbance in this region of the infrared spectrum of wood is primarily due to carbohydrates (Table 2). A lower absorptivity in this region indicates that the amount of carbohydrates in Specimens No. 1 and 2 is less than in the modern wood. Because of microbial or geothermal decomposition of the carbohydrates, bands assigned to lignin show up in this region. The difference in the amount of carbohydrates is supported by the chemical analysis. No carbohydrates could be detected in Specimen No. 2, whereas holocellulose was

TABLE 2. *Assignment of bands in the infrared spectrum of wood (Modified from Michel et al. 1965)*

Frequency (cm^{-1})	Assignment
3600–3200	Hydrogen-bonded OH stretch
2980	CH stretch
2945	CH_2 antisymmetrical stretch
2914–2870	CH stretch
2850	CH_2 stretch
1730–1725	C = O stretch of acetyl or – COOH
1660	Lignin
1635	Adsorbed water
1600	Lignin
1512	Lignin
1460	Lignin and CH_2 symmetrical bending on pyran ring
1425	CH_2 scissor vibrations in cellulose
1370	CH bending vibration in cellulose and hemicellulose
1333	OH in plane bending vibration in cellulose and hemicellulose
1320	CH_2 wagging vibration in cellulose
1260	Lignin
1230	Lignin
1160	COC stretch vibration in cellulose and hemicellulose
1110	OH association band in cellulose and hemicellulose
1050	CO stretch in cellulose and hemicellulose
1030	As 1050
990	As 1050
900	Anomeric carbon group frequency in cellulose and hemicellulose
825	Lignin

present in Specimen No. 1. The absence of carbohydrates in sample No. 2 is also indicated by the absence of absorbance at 900 cm^{-1} in its infrared spectrum (Fig. 17c). This band is attributed to C_1 group frequency in cellulose and hemicellulose, I (Barker et al. 1954; Bellamy 1958). A shoulder in the infrared spectrum of Specimen No. 1 at 900 cm^{-1} indicates the presence of carbohydrates (Fig. 17b).



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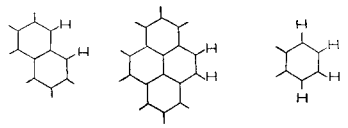
The infrared spectrum of α-cellulose prepared from Specimen No. 1 is compared with the spectra of cotton cellulose and of amorphous cellulose (cotton cellulose milled in a ball mill for 7 days) in Fig. 18. The spectrum of the α-cellulose resembles more closely that of amorphous cellulose (Taniguchi et al. 1965). The cellulose in the ancient pine has therefore lost its crystallinity. The infrared spectra of amorphous cellulose and α-cellulose differ in the carboxyl region at 1700–1730 cm^{-1}. This is probably due to carboxyl groups that are likely to be produced during α-cellulose preparation. The carboxyl groups in the amorphous cellulose, shown by the band at 1730 cm^{-1}, were produced during milling (Wayman and Azhar, unpublished data). A shoulder at 1512 cm^{-1} in the infrared spectrum of the α-cellulose indicates the presence of some residual lignin in the α-cellulose.

Methoxyl and phenolic hydroxyl groups are present in the ancient wood samples as shown by the bands at 1275 and 1225 cm^{-1} (Fig. 17b and c), but the methoxyl band is weaker and the phenolic hydroxyl band is stronger in the ancient wood samples than in modern conifer wood. This accords with the chemical analysis. The relatively low absorbency of the carboxyl band at 1700–1730 cm^{-1} shows that acetyl groups were lost during aging (Table 2).

The infrared spectra of the ancient woods are different from that of the modern wood in the region 1400–1500 cm^{-1}. The bands in this region are mainly attributed to CH and CH_2 groups. These differences could be due to the higher lignin content.

The strong band at 838 cm^{-1} in Specimen No. 1 (Fig. 17b) indicates the differences in substitution pattern on the benzene ring in the two samples. There are normally three bands at 860, 820 and 750 cm^{-1} in coal-like materials. These are assigned, respectively, to out-of-plane vibrations of aromatic CH groups, one isolated II, two adjacent III, and four adjacent IV.



II III IV

The relative intensity of the bands may give an indication of the degree of condensation of aromatic clusters.

The infrared spectra of Specimens No. 1 and 2 and milled spruce wood lignin can be compared from Figs. 17 and 19a. Qualitatively, the spectra are similar. It is difficult to compare the spectrum of Specimen

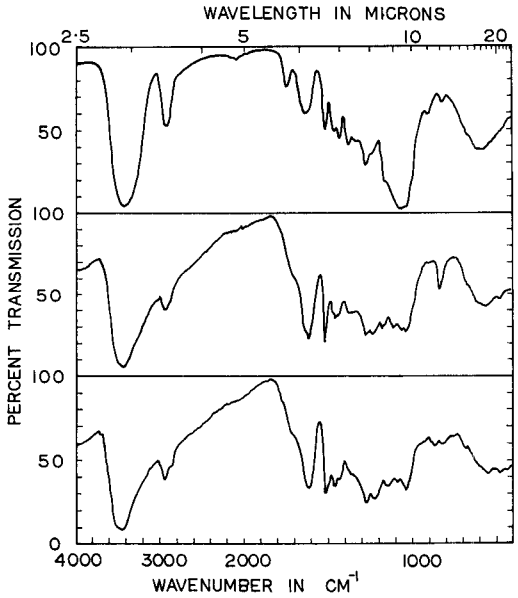


FIG. 17. Infrared spectra top to bottom: (a) Spruce groundwood (b) Specimen No. 1 (c) Specimen No. 2.

TABLE 3. *Assignment of bands in the infrared spectrum of lignin.*

Frequency (cm^{-1})	Assignment
3420	Bonded OH stretch (Bellamy 1958)
2920	CH in OCH_3 and side chain (Bellamy 1958; Bolker and Sommerville 1963; and Liange et al. 1960)
2820	CH_2 stretch
1712	C = O stretch, β-keto or carboxyl (Bolker and Sommerville 1963; Hergert 1960)
1660	C = O of conjugated carbonyl (Bolker and Sommerville 1963; Kolbe and Ellefsen 1962)
1512	Aromatic ring (Bolker and Sommerville 1963; Hergert 1960)
1462	CH deformation (Bland and Logan 1965; Durie et al. 1960; Liange et al. 1960)
1425	CH bending (Bolker and Sommerville 1963; Durie et al. 1960)
1360	OH in plane bend (Bolker and Sommerville 1963; Kolbe and Ellefsen 1962)
1275	OCH_3 (Durie et al. 1960)
1225	Phenolic OH (Durie et al. 1960)
1155	Unassigned (1:2:4 substitution?)
1120	Unassigned (aromatic ether COC or asymmetric stretch vibration in dialkyl ether linkage) (Bolker and Sommerville 1963)
1082	CO deformation, aliphatic ether or hydroxyl (Hergert 1960)
1043	CO deformation, hydroxyl (Bolker and Sommerville 1963; Hergert 1960) COC symmetric stretch in dialkyl ether
857	CH, out of plane bending, one H, aromatic ring (Hergert 1960)
815	CH, out of plane bending, two H, aromatic ring (Bellamy 1958)

TABLE 4. *A/A_{1512} of different bands in the infrared spectra of sample No. 2 and modern spruce milled wood lignin*

Wavenumbers cm^{-1}	1710	1512*	1470	1430	1370	1275	1225	1140	1090	1035	860	820
Sample No. 2	0.35	1.00	0.86	0.74	0.64	1.10	1.01	0.75	0.65	0.78	0.15	0.12†
Milled spruce lignin	0.24	1.00	0.64	0.59	0.42	1.21	0.83	0.87	0.75	0.88	0.88	0.05

* A_{1512} represents the aromatic ring.
† In Sample No. 2 this band appears at 838.

No. 1 with that of the milled wood lignin quantitatively because Specimen No. 1 has a substantial amount of carbohydrates. A quantitative comparison of Specimen No. 2 and milled spruce lignin is given in Table 4.

The nature of the carbonyl groups at around 1700–1750 cm^{-1} is different in the ancient redwood from those in spruce lignin. The carbonyl groups in the redwood appear at a lower wavenumber, which suggests conjugation with the aromatic ring. Demethylation is indicated by the band at 1275 cm^{-1}. The redwood has more phenolic hydroxyl groups than the spruce lignin as shown by the band at 1225 cm^{-1}. The bands in the region 1000–1200 cm^{-1} generally are less intense in the redwood spectrum than in the spruce lignin spectrum. These bands represent mixed vibrations of C-C and C-O bands in ether linkages and alcoholic hydroxyl groups (Table 3). Therefore such functional groups have undergone considerable change during the millennia.

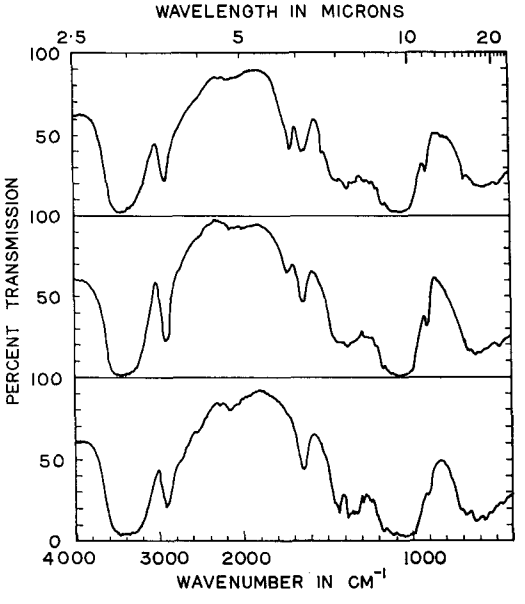
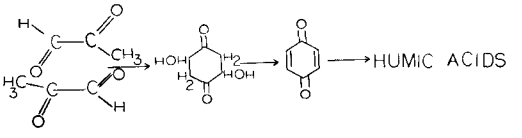


FIG. 18. Infrared spectra top to bottom: (a) α-cellulose from Specimen No. 1 (b) Amorphous cellulose from milled cotton linters (c) Cellulose from cotton linters.

The relation of these ancient woods to coal

Generally speaking, the coalified plant may be said to have gone first through a process of peat formation. When these deposits became buried under sedimentary matter, the peat changed to lignite or brown coal, which probably under the influence of mainly geothermal effects was transformed into bituminous coal and finally to anthracite. The conversion takes place through humic acids. There are different views of the conversion of cellulose and lignin into humic acids. Some studies have suggested that cellulose is not directly involved in the formation of humic substances but serves only as a nutrient for microorganisms. The formation of humic acids can probably be explained by the transformation of lignin. Lignin is first transformed into methoxyl-containing humic acids, which then form methoxyl-free humic acids and ultimately coal through humin, whereas cellulose is mainly converted to CO_2, CH_4 and aliphatic acids on attack by microorganisms. However, methyl glyoxal (pyruvic aldehyde) can be formed from carbohydrates which can easily aromatize forming quinones, and then ultimately the quinones form humic acids as in V (Stereenson and Butler 1969):



The infrared spectrum of a sample of humic acid, a natural product extracted

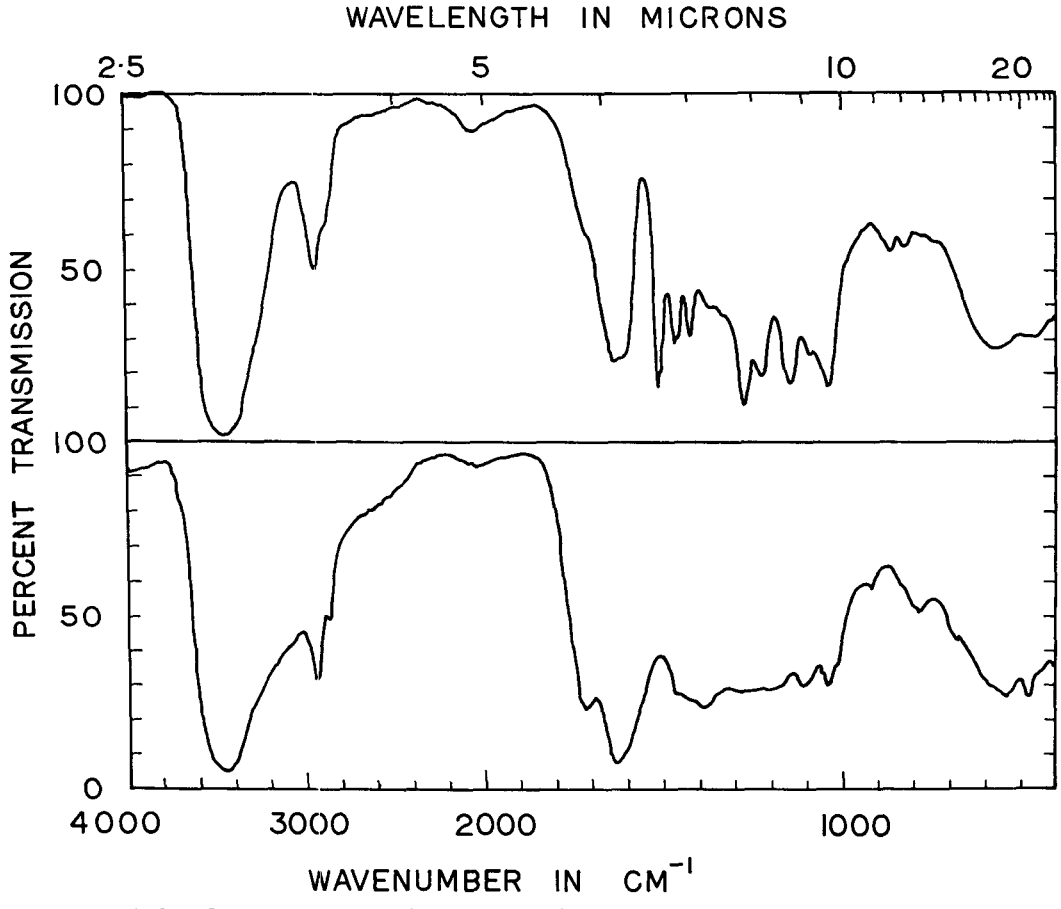


FIG. 19. Infrared spectra. Upper: (a) Spruce milled wood lignin. Lower: (b) Humic acid, from Aldrich Chemical Company.

from soil obtained from Aldrich Chemicals Company, is shown in Figure 19b. The spectra of Specimens No. 1 and 2 do not resemble that of this humic acid or of humic acids from other sources reported in the literature (Elofson 1957; Kinney and Doucette 1958).

Comparison of the infrared spectra of Specimens No. 1 and 2 with that of peatwood, brown coal, bituminous coal and anthracite (Kinney and Doucette 1958) suggests that these samples rank somewhere near peatwood.

A comparison of analyses of coal-forming materials shown in Table 5 with the values given in Table 1 shows an elementary composition between peat and brown coal, but a very much higher methoxyl content than is reported for either of these substances.

TABLE 5. *Analysis of coals (in weight per cent; (Blom 1960)*

Material	C	H	O	OCH_3
Peat	60.0	4.9	33.9	0.9
Brown coal	65.5	5.1	27.8	1.1
Lignite	69.6	4.6	21.9	—
	71.7	4.9	22.6	0.4
	75.9	5.3	16.2	0.3
Hard coal	79.5	5.5	11.1	0
	80.2	4.9	13.4	0
	85.5	5.3	7.9	0
	90.9	4.1	2.0	0

CONCLUSIONS

1. Specimens of wood obtained from rubble ore in iron mines in northern Quebec

were shown to be white pine of about 10^7 years and a species from the Cupressaceae-Taxodiaceae families, probably redwood, of about 10^8 years old.

2. The morphology of the pinewood was fairly well preserved. Tracheids maintained their tubular structure and exhibited microfibrillar structure. Rays clearly showed fenestriform pitting.

3. The morphology of the 100-million-year-old conifer was preserved to a lesser extent. Tracheid lumina, pitting and microfibrillar structure have disappeared, but the rays could readily be identified and contained resin beads.

4. The ancient pinewood has lost most, but not all, of its carbohydrate. The residual cellulose has lost its crystalline structure. The lignin is extensively demethylated.

5. The 100-million-year-old conifer has lost essentially all of its carbohydrate material and behaves as though it is nearly all lignin. The lignin is about one-third demethylated. There has been extensive splitting of lignin ether linkages and loss of alcoholic hydroxyl groups.

6. There is some evidence of condensed ring structures similar to those found in peat in the ancient pinewood, and this may be characterized as in an early stage of transformation to coal. However, the absence of condensed ring structures in the older sample, and the presence of a high methoxyl content are significantly different features from those found in any of the coal-forming substances.

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